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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → Excimer fluorescence is used to study conformational statistics and aggregation in miscible and immiscible blends of polystyrene with poly(vinyl methyl ether). At low polystyrene concentration in miscible blends, excimer fluorescence of isolated polystyrene chains is analyzed in terms of a one-dimensional random walk of the migrating singlet exciton. At high concentration in miscible blends the energy migration is three-dimensional. Knowledge of the fluorescence behavior for miscible blends is used to determine the phase composition for phase separated blends.		

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STATEMENT OF THE PROBLEM STUDIED

The increasing costs associated with the development of a new commercial polymer based upon a new monomer or polymerization process have made such efforts prohibitively expensive except for specialty polymers. As a result, there has been considerable effort in recent years devoted to the study of physical polymer blends or alloys. In principle, the thermomechanical properties of such materials may be optimized by judicious choice of existing homopolymers. In order for such an approach to be successful, however, the degree of mixing must be characterized on the molecular level. This has been the major objective of the research performed under this contract.

All of the work has been done on blends of polystyrene (PS) with poly(vinylmethylether) (PVME). This combination has the interesting property of yielding a miscible one-phase system when solvent cast from toluene but an immiscible two-phase system when cast from tetrahydrofuran. Thus, both morphologies may be easily prepared. Moreover, a transition from one to two phase behavior may be obtained by heating the miscible blend through the lower critical solution temperature. As a result of the ease of manipulation of the morphology, considerable effort has been devoted to the study of the thermodynamics of PS/PVME blends.

In spite of the widespread interest, the classical techniques employed are, in general, relatively insensitive to the details of the blend morphology on the segmental level. Such information may be obtained, however, using excimer fluorescence. This method has been used in a series of papers on blends of poly(2-vinylnaphthalene) (P2VN) with various poly(alkylmethacrylates) (1-6). These studies have included investigation of the effects of solubility parameter differences between the fluorescent guest polymer

and the nonfluorescent host polymer (1,2), guest concentration (2,4,5), molecular weight of both host and guest (3) and the temperature at which the polymer blend is solvent cast (4). In these studies excimer fluorescence has been demonstrated to provide the required information on local aggregation of the guest aromatic vinyl polymer in the immiscible host polymer matrix. Unfortunately, there was insufficient classical information on the P2VN blend thermodynamics with which to compare the fluorescence results. This, of course, is not a problem for the PS/PVME blend.

Although excimer fluorescence provides the direct information on the segment distribution we are seeking, interpretation of the fluorescence results requires analytical models of the photophysical processes by which absorbed energy is localized at the excimer forming sites. This has been the subject of a preliminary study in which a strictly one dimensional random walk model was developed to describe singlet exciton migration in the aromatic vinyl polymers (7). The model applies to isolated guest chains which are dispersed at high dilution in a miscible blend.

The application of this model to the low concentration miscible PS/PVME blends is the subject of the first of two major efforts in research supported by this contract. The second is the development of a simple energy migration model to treat the highly concentrated miscible and immiscible blends. Both studies are described in the next section.

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SUMMARY OF THE MOST IMPORTANT RESULTS

Excimer fluorescence was employed in two major studies on the polystyrene/poly(vinyl methyl ether) blends during the course of the contract. In the first study excimer fluorescence was used to monitor the conformational properties of and energy migration in the polystyrene guest dispersed at low concentration in miscible blends with the poly(vinyl methyl ether) host (8). Fluorescence spectra of monodisperse polystyrene samples with molecular weights ranging from 2200 to 390,000 were taken at temperatures between 286 K and 323 K. Using the one-dimensional random walk model developed by Fitzgibbon (7), the temperature dependence of the concentration of trans-trans meso dyads was obtained from measurements of the ratio of excimer-to-monomer emission intensities. The results were compared with those from rotational isomeric state calculations using chains that have 30% meso dyads. Good agreement was found for temperatures below 303 K but not at higher temperatures. One possible explanation for this is that there is a decrease in the size of the polystyrene coil caused by unfavorable thermodynamic interactions as the blend approaches the lower critical solution temperature.

In the second study a relatively simple three-dimensional energy migration model was developed and used to explain the dependence of the ratio of excimer to monomer fluorescence on concentration for miscible polystyrene/poly(vinyl methyl ether) blends cast from toluene (9). The model is based on a lattice approach for the determination of the dependence of the rate of energy migration and the number of excimer forming sites on concentration. It is applicable at concentrations for which the rate of off chain transfers is equal to the rate of down chain transfer. It was found that, although singlet energy migration is important at high polystyrene concentrations,

excitons make only a small number of hops before emission or trapping at an excimer forming site.

In addition, the experimental results for miscible blends have been utilized in a quantitative analysis of the concentration dependence of the ratio for immiscible blends cast from tetrahydrofuran. A two phase model was applied, in which it is assumed that energy migration does not occur between the phases. The volume fractions of polystyrene in the rich and lean phases have been obtained from application of this model to the fluorescence data.

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